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(54) DETERGENT COMPOSITIONS

(71) We, THE PROCTER & GAMBLE COMPANY, a Company organised under the laws of the State of Ohio, United States of America, of 301 East Sixth Street, Cincinnati, Ohio 45202, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to granular built laundry detergent compositions which provide simultaneous laundering and softening of textiles during conventional fabric laundering operations. Such compositions employ a combination of non-soap synthetic detergent compounds, organic or inorganic detergent builders and particular smectite clay compounds having particular cation exchange characteristics.

Various clays materials have been used in many different types of detergent systems for widely differing purposes. Clays, for example, have been disclosed for use as builders (Schwartz and Perry, *Surface Active Agents*, Interscience Publishers, Inc., 1949, pp. 232 and 299); as water-softeners (British Patent 461, 221); as anti-caking agents (U.S. Patents 2,625,513 and 2,770,600); as suspending agents (U.S. Patents 2,594,257, 2,594,258 and 2,920,045); and as fillers (U.S. Patent 2,708,185).

It is also well known that some clay materials can be deposited on fabrics to impart softening and antistatic properties thereto. Such clay deposition is generally realized by contacting fabrics to be so treated with aqueous clay suspensions (See, for example, U.S. Patents 3,033,699 and 3,594,221).

Attempts, however, to incorporate clay materials into *built* detergent systems for the purpose of providing simultaneous fabric laundering and softening have not been entirely successful. Conventional detergent builders tend to retard or inhibit the tendency of clay materials to deposit on fabric surfaces, such deposition being necessary to realize the desired fabric softening results. Furthermore, to provide the requisite uniform deposition of clay material onto fabrics being laundered, the clay material must be thoroughly and quickly dispersed throughout the fabric laundering solution during the relatively brief wash cycle.

Some of these difficulties of providing through-the-wash clay softening have been resolved by using conventional fabric softening agents such as isostearic acid or polyamine or polyquaternary ammonium compounds in combination with clay in built detergent formulations (See U.S. Patents 3,594,212 and 3,625,905). The dispersability problem can be alleviated somewhat by adding to laundering solutions built *liquid* detergent compositions wherein clay is suspended and therefore more easily dispersed (See U.S. Patent 2,920,045). However, such liquid heavy-duty built laundry compositions do not provide the convenience associated with *granular* laundry products.

Accordingly, it is an object of the present invention to provide granular built laundry detergent compositions which can yield simultaneous fabric laundering and fabric softening.

It has surprisingly been discovered that by using particular types of clay having particular cation exchange characteristics, these objectives can be realized and built

granular fabric laundering and softening compositions can be obtained which are unexpectedly superior to similar compositions known to the prior art.

The present invention provides granular built laundry detergent compositions comprising: (a) from 2% to 30% by weight of a non-soap synthetic detergent compound selected from anionic synthetic detergents, ampholytic synthetic detergents, zwitterionic synthetic detergents and mixtures thereof; (b) from 10% to 60% by weight of one or more organic and/or inorganic detergent builder salts; and (c) from 1% to 50% by weight of a fabric-softening agent that is an expandable, three layer smectite-type clay having an ion exchange capacity of at least 50 meq/100g, such compositions providing a solution pH of from 7 to 12 when dissolved in water at a concentration of 0.12% by weight. The present invention also provides a process for concurrently cleansing and softening fabrics comprising contacting said fabrics with an effective amount (e.g., from 0.02% to 2% by weight) of a laundry detergent composition as described above, for example by laundering said fabrics in an aqueous laundry bath containing the said composition.

Compositions of this invention comprise three essential components—synthetic non-soap detergent, builder salt and clay. Each component is described in detail as follows:

Synthetic Detergent.

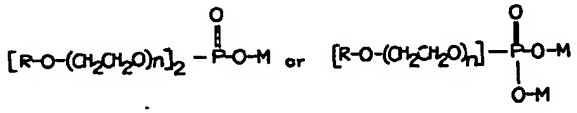
From 2% to 30% by weight, preferably from 5% to 20% by weight, of the compositions of the invention comprise a non-soap synthetic detergent selected from anionic synthetic detergents, ampholytic synthetic detergents, zwitterionic synthetic detergents and mixtures thereof. This component of the composition is preferably constituted by one or more anionic synthetic detergents. Examples of synthetic detergents of these types are described as follows:

Anionic Detergents.

Anionic synthetic detergents include water-soluble salts, particularly the alkali metal salts, of organic sulphuric reaction products having in their molecular structure an alkyl group containing from 8 to 22 carbon atoms and a moiety selected from sulphonic acid and sulphuric acid ester moieties. (Included in the term alkyl is the alkyl portion of acyl moieties.) Examples of this group of synthetic detergents which form a part of the preferred built detergent compositions of the present invention are: the sodium and potassium alkyl sulphates, especially those obtained by sulphating the higher alcohols (C_8—C_{18} carbon atoms) produced by reducing the glycerides of tallow or coconut oil; sodium and potassium alkyl benzene sulphonates, in which the alkyl group contains from 9 to 20 carbon atoms in straight chain or branched-chain configuration, for example those of the type described in United States Patents Numbers 2,220,099 and 2,477,383 (especially valuable are linear straight chain alkyl benzene sulphonates in which the average of the alkyl groups is about 11.8 carbon atoms and commonly abbreviated as $C_{11.8}$LAS): sodium alkyl glyceryl ether sulphonates, especially those ethers of higher alcohols derived from tallow and coconut oil: sodium coconut oil fatty acid monoglyceride sulphonates and sulphates; sodium and potassium salts of sulphuric acid esters of the reaction product of one mole of a higher fatty alcohol (for example tallow or coconut oil alcohols) and about 1 to 6 mols of ethylene oxide; sodium and potassium salts of alkyl phenol ethylene oxide ether sulphates with 1 to 10 units of ethylene oxide per molecule and in which the alkyl groups contain from 8 to 12 carbon atoms.

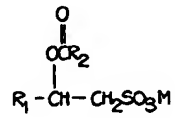
Anionic phosphate surfactants are also useful in the present invention. These are surface active materials having substantial detergent capability in which the anionic solubilizing group connecting hydrophobic moieties is an oxy acid of phosphorus. The more common solubilizing groups, of course, are —SO_4H and SO_3H. Alkyl phosphate esters such as $(R—O)_2PO_2H$ and $ROPO_3H_2$ in which R represents an alkyl chain containing from 8 to 20 carbon atoms are useful herein.

These phosphate esters can be modified by including in the molecule from one to about 40 alkylene oxide units, for example, ethylene oxide units. The formulae for these modified phosphate anionic detergents are



in which R represents an alkyl group containing from about 8 to 20 carbon atoms, or an alkylphenyl group in which the alkyl group contains from about 8 to 20 carbon atoms, and M represents a soluble cation such as hydrogen, sodium, potassium, ammonium or substituted ammonium; and in which n is an integer from 1 to 40.

Another class of suitable anionic organic detergents particularly useful in this invention includes salts of 2-acyloxyalkane-1-sulphonic acids. The salts have the formula



where R_1 is alkyl having from 9 to 23 carbon atoms (forming with the two carbon atoms an alkane group); R_2 is alkyl having from 1 to 8 carbon atoms; and M is a water-soluble cation.

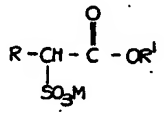
The water-soluble cation, M, in the hereinbefore described structural formula can be, for example, an alkali metal cation (for example sodium, potassium, lithium), ammonium or substituted-ammonium cation. Specific examples of substituted ammonium cations include: methyl-, dimethyl-, and trimethyl- ammonium cations and quaternary ammonium cations such as tetramethyl-ammonium and dimethyl piperidinium cations and those derived from alkylamines such as ethylamine, diethylamine, triethylamine and mixtures thereof.

Specific examples of beta-acyloxy-alkane-1-sulphonates, or alternatively 2-acyloxy-alkane-1-sulphonates, useful herein include the sodium salt of 2-acetoxy-tridecane-1-sulphonic acid; the potassium salt of 2-propionyloxy-tetradecane-1-sulphonic acid; the lithium salt of 2-butanoyloxy-tetradecane-1-sulphonic acid; the sodium salt of 2-pentanoyloxy-pentadecane-1-sulphonic acid; the sodium salt of 2-acetoxy-hexadecane-1-sulphonic acid; the potassium salt of 2-octanoyloxytetradecane-1-sulphonic acid; the sodium salt of 2-acetoxy-heptadecane-1-sulphonic acid; the lithium salt of 2-acetoxy-octadecane-1-sulphonic acid; the potassium salt of 2-acetoxy-nonadecane-1-sulphonic acid; the sodium salt of 2-acetoxy-uncosane-1-sulphonic acid; the sodium salt of 2-propionyloxy-docosane-1-sulphonic acid; the isomers thereof.

Preferred beta-acyloxy-alkane-1-sulphonate salts herein are the alkali metal salts of beta-acetoxy-alkane-1-sulphonic acids corresponding to the above formula wherein R_1 is an alkyl having from 12 to 16 carbon atoms; these salts being preferred because of their excellent cleaning properties and ready availability.

Typical examples of the above described beta-acetoxy alkane-sulphonates are described in the literature: Belgium Patent 650,323 discloses the preparation of certain 2-acyloxy alkanesulphonic acids. Similarly, U.S. Patents 2,094,451 (Guenther et al) and 2,086,215 (DeGroote) disclose certain salts of beta-acetoxy alkanesulphonic acids.

Another preferred class of anionic detergent compounds herein, both by virtue of superior cleaning properties and low sensitivity to water hardness (Ca^{++} and Mg^{++} ions) are the alkylated α-sulyphocarboxylates, containing from 10 to 23 carbon atoms and having the formula



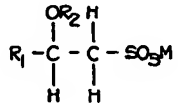
wherein R is C_8 to C_{20} alkyl, M is a water-soluble cation as hereinbefore disclosed, preferably a sodium ion, and R' is a C_1—C_4 alkyl, e.g., methyl, ethyl, propyl and butyl. These compounds are prepared by the esterification of α-sulphonated carboxylic acids, which are commercially available, using standard techniques. Specific examples of the alkylated α-sulphocarboxylates preferred for use herein include:

Ammonium methyl-α-sulphopalmitate,
Triethanolammonium ethyl-α-sulphostearate,
sodium methyl-α-sulphopalmitate,
sodium ethyl-α-sulphopalmitate,

sodium butyl-α-sulphostearate,
potassium methyl-α-sulpholaurate,
lithium methyl-α-sulpholaurate,

as well as mixtures thereof.

A preferred class of anionic organic detergents are the β-alkyloxy alkane sulphonates. These compounds have the following formula:



where R_1 is a straight chain alkyl group having from 6 to 20 carbon atoms, R_2 is a lower alkyl group having from 1 (preferred) to 3 carbon atoms, and M is a water-soluble cation as hereinbefore described.

Specific examples of β-alkyloxy alkane sulphonates, or alternatively 2-alkyloxy-alkane-1-sulphonates, having low hardness (calcium ion) sensitivity useful herein to provide superior cleaning levels under household washing conditions include:

potassium-β-methoxydecanesulphonate,
sodium 2-methoxytridecanesulphonate,
potassium 2-ethoxytetradecylsulphonate,
sodium 2-isopropoxyhexadecylsulphonate,
lithium 2-t-butoxytetradecylsulphonate,
sodium β-methoxyoctadecylsulphonate, and
ammonium β-n-propoxydodecylsulphonate.

Other synthetic anionic detergents useful herein are alkyl ether sulphates. These materials have the formula $RO(C_2H_4O)_x SO_3M$ wherein R is alkyl or alkenyl having from 10 to 20 carbon atoms, x is from 1 to 30, and M is a water-soluble cation as defined hereinbefore. The alkyl ether sulphates useful in the present invention are condensation products of ethylene oxide and monohydric alcohols having from 10 to 20 carbon atoms. Preferably, R has 12 to 18 carbon atoms. The alcohols can be derived from fats, for example, coconut oil or tallow, or can be synthetic. Lauryl alcohol and straight chain alcohols derived from tallow are preferred herein. Such alcohols are reacted with from 1 to 30, and especially 6, molar proportions of ethylene oxide and the resulting mixture of molecular species, having, for example, an average of 6 moles of ethylene oxide per mole of alcohol, is sulphated and neutralized.

Specific examples of alkyl ether sulphates of the present invention are: sodium coconut alkyl ethylene glycol ether sulphate; lithium tallow alkyl triethylene glycol ether sulphate; and sodium tallow alkyl hexaoxyethylene sulphate.

Preferred herein for reasons of excellent cleaning properties and ready availability are the alkali metal coconut- and tallow-alkyl oxyethylene ether sulphates having an average of from 1 to 10 oxyethylene moieties. The alkyl ether sulphates of the present invention are known compounds and are described in U.S. Patent 3,332,876 to Walker.

Additional examples of anionic non-soap synthetic detergents which come within the terms of the present invention are the reaction product of fatty acids esterified with isethionic acid and neutralized with sodium hydroxide where, for example, the fatty acids are derived from coconut oil; sodium or potassium salts of fatty acid amides of methyl tauride in which the fatty acids, for example, are derived from coconut oil. Other anionic synthetic detergents of this variety are set forth in United States Patents 2,486,921; 2,486,922; and 2,396,278.

Additional examples of anionic, non-soap, synthetic detergents, which come within the terms of the present invention, are the compounds which contain two anionic functional groups. These are referred to as di-anionic detergents. Suitable di-anionic detergents are the disulphonates, disulphates, or mixtures thereof which may be represented by the following formulae:

$$R(SO_3)_2M_2, \quad R(SO_4)_2M_2, \quad R(SO_3)(SO_4)M_2,$$

where R is an acyclic aliphatic hydrocarbyl group having 15 to 20 carbon atoms and M is a water-solubilizing cation, for example, the C_{15} to C_{20} disodium 1,2-alkyldisulphates,

C_{15} to C_{20} dipotassium 1,2-alkyldisulphonates or disulphates, disodium 1,9-hexadecyl disulphates, C_{15} to C_{20} disodium-1,2-alkyldisulphonates, disodium 1,9-stearyldisulphates and 6,10-octadecyldisulphates.

The aliphatic portion of the disulphates or disulphonates is generally substantially linear, thereby imparting desirable bio-degradable properties to the detergent compound.

The water-solubilizing cations include the customary cations known in the detergent art, i.e., the alkali metals, and the ammonium cations, as well as other metals in group IIA, IIB, IIIA, IVA and IVB of the Periodic Table except for boron. The preferred water-solubilizing cations are sodium or potassium. These dianionic detergents are more fully described in British Letters Patent 1,151,392.

Still other anionic synthetic detergents include the class designated as succinamates. This class includes such surface active agents as disodium N-octadecylsulphosuccinamate: tetrasodium N-(1,2-dicarboxyethyl)-N-octadecylsulpho-succinamate; diamyl ester of sodium sulphosuccinic acid: dihexyl ester of sodium sulphosuccinic acid: dioctyl esters of sodium sulphosuccinic acid.

Other suitable anionic detergents utilizable herein are olefin sulphonates having from 12 to 24 carbon atoms. The term "olefin sulphonates" is used herein to mean compounds that can be produced by the sulphonation of α-olefins by means of uncomplexed sulphur trioxide, followed by neutralization of the acid reaction mixture in conditions such that any sultones which have been formed in the reaction are hydrolyzed to give the corresponding hydroxy-alkane-sulphonates. The sulphur trioxide can be liquid or gaseous, and is usually, but not necessarily, diluted by inert diluents, for example by liquid SO_2 or chlorinated hydrocarbons, when used in the liquid form, for example by air, nitrogen or gaseous SO_2, when used in the gaseous form.

The α-olefins from which the olefin sulphonates are derived are mono-olefins having 12 to 24 carbon atoms, preferably 14 to 16 carbon atoms. Preferably, they are straight chain olefins. Examples of suitable 1-olefins include 1-dodecene: 1-tetradecene: 1-hexadecene: 1-octadecene: 1-eicosene and 1-tetracosene.

In addition to the true alkene sulphonates and a proportion of hydroxy-alkane-sulphonates, the olefin sulphonates can contain minor amounts of other materials, such as alkene disulphonates depending upon the reaction conditions, proportion of reactants, the nature of the starting olefins and impurities in the olefin stock and side reactions during the sulphonation process.

A specific anionic detergent which has also been found excellent for use in the present invention is described more fully in the U.S. Patent 3,332,880 of Phillip F. Pflaumer and Adrian Kessler.

Of all the above-described types of anionic surfactants, preferred compounds include sodium linear alkyl benzene sulphonate wherein the alkyl chain averages from about 10 to 18, more preferably about 12, carbon atoms in length, sodium tallow aikyl sulphate, 2-acetoxy-tridecane-1-sulphonic acid; sodium methyl-α-sulphopalmitate; sodium β-methoxyoctadecylsulphonate; sodium coconut alkyl ethylene glycol ether sulphonate; the sodium salt of the sulphuric acid ester of the reaction product of one mole of tallow alcohol and three moles of ethylene oxide; and mixtures thereof.

Ampholytic Synthetic Detergents.

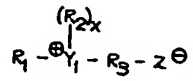
Ampholytic synthetic detergents can be broadly described as derivatives of aliphatic or aliphatic derivatives of heterocyclic secondary and tertiary amines in which the aliphatic radical may be straight chain or branched and wherein one of the aliphatic substituents contains from about 8 to 18 carbon atoms and at least one contains an anionic water-solubilizing group, for example, carboxy, sulphonate, sulphato. Examples of compounds falling within this definition are: sodium 3-(dodecylamino)-propionate, sodium 3-(dodecylamino) propane-1-sulphonate, sodium 2-(dodecylamino) ethyl sulphate, sodium 2-(dimethylamino)octadecanoate, disodium 3-(N-carboxymethyldodecylamino)-propane-1-sulphonate, disodium octadecyliminodiazetate, sodium 1-carboxymethyl-2-undecylimidazole, and sodium N,N-bis(2-hydroxyethyl)-2-sulphato-3-dodecoxypropylamine. Sodium 3-(dodecylamino)propane-1-sulphonate is preferred.

Zwitterionic Synthetic Detergents.

Zwitterionic surfactants can be broadly described as derivatives of secondary and tertiary amines, derivatives of heterocyclic secondary and tertiary amines, or derivatives of quaternary ammonium, quaternary phosphonium or tertiary sulphonium compounds. The cationic atom in the quaternary compound can be part of a heterocyclic ring. In all of these compounds there is at least one aliphatic group, straight chain or branched, containing from 3 to 18 carbon atoms and at least one aliphatic substituent containing

an anionic water-solubilizing group, for example, carboxy, sulphonate, sulphato, phosphato, or phosphono. Examples of various classes of zwitterionic surfactants operable herein are described as follows:

1. Compounds corresponding to the general formula



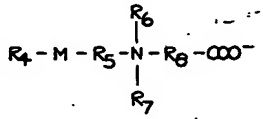
wherein R_1 is alkyl, alkenyl or a hydroxyalkyl containing from 8 to 18 carbon atoms and containing if desired up to about 10 ethylene oxide moieties and/or a glyceryl moiety, Y_1 is nitrogen, phosphorus or sulphur, R_2 is alkyl or monohydroxyalkyl containing 1 to 3 carbon atoms; x is 1 when Y_1 is S, 2 when Y_1 is N or P; R_3 is alkylene or hydroxyalkylene containing from 1 to 5 carbon atoms; and Z is a carboxy, sulphonate, sulphate, phosphate or phosphonate group.

Examples of this class of zwitterionic surfactants include: 3-(N,N-dimethyl-N-hexadecylammonio)-propane-1-sulphonate; 3-(N,N-dimethyl-N-hexadecylammonio)-2-hydroxypropane - 1 - sulphonate; 2 - (N,N - dimethyl - N - dodecylammonio acetate; 3 - (N,N - dimethyl - N - dodecylammonio) propionate; 2 - (N,N - dimethyl - N-octadecylammonio)ethane - 1 - sulphate; 3 - (P,P - dimethyl - P - dodecylphosphonio)-propane - 1 - sulphonate; 2 - (S - methyl - S - tetra - hexadecylsulphonio)ethane - 1-sulphonate; 3 - (S - methyl - S - dodecylsulphonio)propionate; 4 - (S - methyl - S-tetra - decylsulphonio)butyrate; 3 - (N,N - dimethyl - N - 4 - dodecenylammonio)-propane - 1 - sulphonate; 3 - (N,N - dimethyl - N - 2 - diethoxyhexadecylammonio)-propane - 1 - phosphate; and 3 - (N,N - dimethyl - N - 4 - glyceryldodecylammonio)-propionate.

Preferred compounds of this class from a commercial standpoint are 3 - (N,N-dimethyl - N - hexadecylammonio) - 2 - hydroxypropane - 1 - sulphonate; 3 - (N,N-dimethyl - N - alkylammonio) - 2 - hydroxypropane - 1 - sulphonate, the alkyl group being derived from tallow fatty alcohol; 3 - (N,N - dimethyl - N - hexadecylammonio)-propane - 1 - sulphonate; 3 - N,N - dimethyl - N - tetradecylammonio)propane - 1-sulphonate; 3 - (N,N - dimethyl - N - alkylammonio) - 2 - hydroxypropane - 1-sulphonate, the alkyl group being derived from the middle cut of coconut fatty alcohol; 3 - (N,N - dimethyldodecylammonio) - 2 - hydroxypropane - 1 - sulphonate; 4-(N,N - dimethyl - tetradecylammonio)butane - 1 - sulphonate; 4(N,N - dimethyl - N-hexadecylammonio) butane - 1 - sulphonate; 4 - (N,N - dimethyl - hexadecylammonio)butyrate; 6 - (N,N - dimethyl - N - octadecylammonio)hexanoate; 3 - (N,N-dimethyl - N - eicosylammonio) - 3 - methylpropane - 1 - sulphonate; and 6 - (N,N-dimethyl - N - hexadecylammonio)hexanoate.

Means for preparing many of the surfactant compounds of this class are described in U.S. Patents 2,129,264, 2,774,786, 2,813,898, 2,828,332 and 3,529,521 and; German Patent 1,018,421.

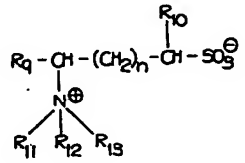
2. Compounds having the general formula:



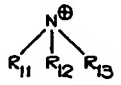
wherein R_4 is an alkyl, cycloalkyl, aryl, aralkyl or alkaryl group containing from 10 to 20 carbon atoms; M is a bivalent radical selected from: aminocarbonyl, carbonylamino, carbonyloxy, aminocarbonylamino, the corresponding thio groupings and substituted amino derivatives; R_5 and R_8 are alkylene groups containing from 1 to 12 carbon atoms; R_6 is alkyl or hydroxyalkyl containing from 1 to 10 carbon atoms; R_7 is selected from R_6 groups, R_4—M—R_5—, and —R_8COOMe wherein R_4, R_5, R_6 and R_8 are as defined above and Me is a monovalent salt-forming cation. Compounds of this type include N,N - bis(oleylamidopropyl) - N - methyl - N - carboxymethylammonium betaine; N,N - bis(stearamidopropyl) - N - methyl - N - carboxymethylammonium betaine; N - (stearamidopropyl) - N - dimethyl - N - carboxymethylammonium betaine; N,N - bis(oleylamidopropyl) - N - (2 - hydroxyethyl) - N - carboxymethylammonium betaine; and N - N - bis - (stearamidopropyl) - N - (2 - hydroxyethyl)-N - carboxymethylammonium betaine. Zwitterionic surfactants of this type are pre-

pared in accordance with methods described in U.S. Patent 3,265,719 and German Auslegerschrift (Published Specification) 1,018,421.

3. Compounds having the general formula:

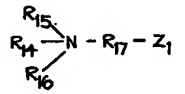


wherein R_9 is an alkyl group, R_{10} is a hydrogen atom or an alkyl group, the total number of carbon atoms in R_9 and R_{10} being from 8 to 16 and



represents a quaternary ammonio group in which each group R_{11}, R_{12} and R_{13} is an alkyl or hydroxyalkyl group or the groups R_{11}, R_{12} and R_{13} are conjoined in a heterocyclic ring and n is 1 or 2. Examples of suitable zwitterionic surfactants of this type include the γ and δ hexadecylpyridino sulphobetaines, the γ and δ hexadecyl γ-picolino sulphobetaines, the γ and δ tetradecyl pyridino sulphobetaines and the hexadecyl trimethylammonio sulphobetaines. Preparation of such zwitterionic surfactants is described in published South African patent application 69/5788.

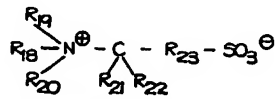
4. Compounds having the general formula



wherein R_{14} is an alkarylmethylene group containing from 8 to 24 carbon atoms in the alkyl chain; R_{15} is selected from R_{14} groups and alkyl and hydroxyalkyl groups containing from 1 to 7 carbon atoms; R_{16} is alkyl or hydroxyalkyl containing from 1 to 7 carbon atoms; R_{17} is alkylene or hydroxyalkylene containing from 1 to 7 carbon atoms and Z_1 is selected from: sulphonate, carboxy and sulphate. Examples of zwitterionic surfactants of this type include 3 - (N - dodecylbenzyl - N,N - dimethylammonio) - propane - 1 - sulphonate; 4 - (N - dodecylbenzyl - N,N - dimethylammonio)butane-1-sulphonate; 3 - (N - hexadecylbenzyl - N,N - dimethylammonio) propane - 1-sulphonate; 3 - (N - dodecylbenzyl - N,N - dimethylammonio)propionate; 4 - (N-hexadecylbenzyl - N,N - dimethylammonio)butyrate; 3 - (N - tetradecylbenzyl - N,N-dimethylammonio)propane - 1 - sulphate; 3 - (N - dodecylbenzyl - N,N - dimethylammonio) - 2 - hydroxypropane - 1 - sulphonate; 3 - [N,N - di(dodecylbenzyl) - N-methylammonio]propane - 1 - sulphonate; 4 - [N,N - di(hexadecylbenzyl) - N-methylammonio]butyrate; and 3 - ([N,N - di(tetradecylbenzyl) - N - methylammonio] 2-hydroxypropane-1-sulphonate.

Zwitterionic surfactants of this type as well as methods for their preparation are described in U.S. Patents 2,697,116; 2,697,656 and 2,669,991 and Canadian Patent 883,864.

5. Compounds having the general formula:



wherein R_{18} is an alkylphenyl, cycloalkylphenyl or alkenylphenyl group containing from 8 to 20 carbon atoms, in the alkyl, cycloalkyl or alkenyl moiety; R_{19} and R_{20} are each aliphatic groups containing from 1 to 5 carbon atoms; R_{21} and R_{22} are each hydrogen

atoms, hydroxyl groups or aliphatic groups containing from 1 to 3 carbon atoms and R_{23} is an alkylene group containing from 2 to 4 carbon atoms.

Examples of zwitterionic surfactants of this type include 3-(N-dodecylphenyl-N,N - dimethylammonio)propane - 1 - sulphonate; 4 - (N - hexadecylphenyl - N,N-dimethyl)butane - 1 - sulphonate; 3 - (N - tetradecylphenyl - N,N - dimethyl-ammonio) - 3,3 - dimethylpropane - 1 - sulphonate and 3 - (N - dodecylphenyl - N,N-dimethylammonio) - 3 - hydroxypropane - 1 - sulphonate. Compounds of this type are described more fully in British Patents 970,883 and 1,046,252.

Of all the above-described types of zwitterionic surfactants, preferred compounds include: 3(N,N - dimethyl - N - alkylammonio) - propone - 1 - sulphonate and 3-(N,N - dimethyl - N - alkylammonio) - 2 - hydroxypropane - 1 - sulphonate wherein in both compounds the alkyl group averages 14.8 carbon atoms in length; 3(N,N-dimethyl - N - hexadecylammonio) - propane - 1 - sulphonate; 3(N,N - dimethyl-N - hexadecylammonio) - 2 - hydroxypropane - 1 - sulphonate; 3 - (N - dodecyl-benzyl - N,N - dimethylammonio) - propane - 1 - sulphonate; (N - dodecylbenzyl-N,N - dimethylammonio)acetate; 3 - (N - dodecylbenzyl - N,N - dimethylammonio)-propionate; 6 - (N - dodecylbenzyl - N,N - dimethylammonio)hexanoate; and (N,N-dimethyl - N)hexadecylammonio)acetate.

Builder Salts.

The detergent compositions of the present invention contain, as an essential component, a polyanionic detergent builder salt. In the present compositions these water-soluble builder salts serve to maintain the pH of the laundry solution in the range of from 7 to 12, preferably from 8 to 11. Furthermore, these builder salts enhance the fabric cleaning performance of the overall compositions while at the same time serve to suspend particulate soil released from the surface of the fabrics and prevent its redeposition on the fabric surfaces. Surprisingly, although the detergency builder salts serve to suspend clay soils of the kaolinite and illite types and prevent their redeposition on fabrics, they do not appear to interfere with the deposition on fabric surfaces of the smectite-type clay softeners used herein. Furthermore, these polyanionic builder salts have been found to cause the smectite-type clays present in the granular detergent formulations of the invention to be readily and homogeneously dispersed throughout the aqueous laundering medium with a minimum of agitation. The homogeneity of the clay dispersion is necessary for the clay to function effectively as a fabric softener, while the ready dispersability allows granular detergent compositions to be formulated.

Suitable detergent builder salts useful herein can be of the poly-valent inorganic and poly-valent organic types, or mixtures thereof. Non-limiting examples of suitable water-soluble, inorganic detergent builder salts include the alkali metal carbonates, borates, phosphates, polyphosphates, tripolyphosphates, bicarbonates, and sulphates. Specific examples of such salts include the sodium and potassium tetraborates, perborates, bicarbonates, carbonates, tripolyphosphates, orthophosphates and hexametaphosphates.

Examples of suitable organic alkaline detergency builder salts are: (1) water-soluble amino polyacetates, for example, sodium and potassium ethylenediamine tetraacetates, nitrilotriacetates and N-(2-hydroxyethyl)nitrilodiacetates; (2) water-soluble salts of phytic acid, for example, sodium and potassium phytates; (3) water-soluble polyphosphonates, including, sodium, potassium and lithium salts of ethane-1-hydroxy-1,1-diphosphonic acid; sodium, potassium and lithium salts of methylenediphosphonic acid.

Additional organic builder salts useful herein include the polycarboxylate materials described in U.S. Patent 2,264,103, including the water-soluble alkali metal salts of mellitic acid. The water-soluble salts of polycarboxylate polymers and copolymers such as are described in U.S. Patent 3,308,067, are also suitable for use herein. It is to be understood that while the alkali metal salts of the foregoing inorganic and organic poly-valent anionic builder salts are preferred for use herein from an economic standpoint, the ammonium, alkanolammonium, for example triethanolammonium ad diethanol-ammonium, water-soluble salts of any of the foregoing builder anions are useful herein.

Mixtures of organic and/or inorganic builders can be used herein. One such mixture of builders is disclosed in Canadian Patent 755,038, for example, a ternary mixture of sodium tripolyphosphate, trisodium nitrilotriacetate and trisodium ethane-1-hydroxy-1,1-diphosphonate.

While any of the foregoing alkaline poly-anionic builder materials are useful herein, sodium tripolyphosphate, sodium nitrilotriacetate, sodium mellitate, sodium

citrate and sodium carbonate are preferred herein for this builder use. Sodium tripolyphosphate is especially preferred herein as a builder both because of its detergency builder activity and its ability to disperse homogeneously and quickly the smectite clays throughout the aqueous laundry media without interfering with clay deposition on the fabric surface. Sodium tripolyphosphate is also especially effective for suspending illite and kaolinite clay soils and retarding their redeposition on the fabric surface.

The detergent builders are used at concentrations of from 10% to 60%, preferably from 20% to 50% by weight of the detergent compositions of this invention.

Clay Compounds.

The third essential component of the present compositions consists of particular smectite clay materials to provide fabric softening concurrently with fabric cleansing. These smectite clays are present in the detergent compositions in amounts from 1% to 50%, preferably from 5% to 15% by weight of the total compositions.

The clay minerals used to provide the softening properties of the instant compositions can be described as expandable, three-layer clays i.e., alumino-silicates and magnesium silicates, having an ion exchange capacity of at least 50 meq/100 g. of clay. The term "expandable" as used to describe clays relates to the ability of the layered clay structure to be swollen or expanded, on contact with water. The three-layer expandable clays used herein are those materials classified geologically as smectites.

There are two distinct classes of smectite-type clays: in the first, aluminium oxide is present in the silicate crystal lattice; in the second class of smectites, magnesium oxide is present in the silicate crystal lattice. The general formulae of these smectites are $A_2(Si_2O_5)_2(OH)_2$ and $Mg_3(Si_2O_5)_2(OH)_2$, for the aluminium and magnesium oxide type clay, respectively. It is to be recognized that the range of the water or hydration in the above formulas can vary with the processing to which the clay has been subjected. This is immaterial to the use of the smectite clays in the present invention in that the expandable characteristics of the hydrated clays are dictated by the silicate lattice structure. Furthermore, atom substitution by iron and magnesium can occur within the crystal lattice of the smectites, while metal cations such as Na+, Ca++, as well as H+, can be co-present in the water of hydration to provide electrical neutrality. Except as mentioned below, such cation substitutions are immaterial to the use of the clays herein since the desirable physical properties of the clays are not substantially altered thereby.

The three-layer, expandable alumino-silicates useful herein are further characterized by a dioctahedral crystal lattice, while the expandable three-layer magnesium silicates have a trioctahedral crystal lattice.

As noted hereinabove, the clays employed in the compositions of this invention contain cationic counterions such as protons, sodium ions, potassium ions, calcium ions and magnesium ions. It is customary to distinguish between clays on the basis of one cation predominantly or exclusively absorbed. For example, a sodium clay is one in which the absorbed cation is predominantly sodium. Such absorbed cations can become involved in exchange reactions with cations present in aqueous solutions. A typical exchange reaction involving a smectite-type clay is expressed by the following equation:

$$\text{smectite clay (Na)} + NH_4OH \rightleftarrows \text{smectite clay } (NH_4) + NaOH$$

Since the foregoing equilibrium reaction, one equivalent weight of ammonium ion replaces an equivalent weight of sodium, it is customary to measure exchange capacity (sometimes termed "base exchange capacity") in terms of milliequivalents per 100 g. of clay (meq./100g.). The cation exchange capacity of clays can be measured in several ways, including by electrodialysis, by exchange with ammonium ion followed by titration or by a methylene blue procedure, all as fully set forth in Grimshaw, "The Chemistry and Physics of Clays", pp. 264—265, Interscience (1971). The cation exchange capacity of a clay mineral relates to such factors as the expandable properties of the clay, the charge of the clay, which, in turn, is determined at least in part by the lattice structure. The ion exchange capacity of clays varies widely in the range from about 2 meq/100 g. for kaolinites to about 150 meq/100 g., and greater, for certain clays of the montmorillionite variety. Illite clays have an ion exchange capacity somewhere in the lower portion of the range, i.e., about 26 meq/100 g. for an average illite clay.

It has been determined that illite and kaolinite clays, with their relatively low ion exchange capacities, are not useful in the instant compositions. Indeed, such illite and

kaolinite clays constitute a major component of clay soils and, as noted above, are removed from fabric surfaces by means of the instant compositions. However, smectites, such as nontronite, having an ion exchange capacity of approximately 50 meq/100 g., saponite, which has an ion exchange capacity of around 70 meq/100 g., and montmorillonite, which has an ion exchange capacity greater than 70 meq/100 g., have been found to be useful in the compositions of the invention in that they are deposited on the fabrics to provide the desired softening benefits. Accordingly, clay minerals useful herein can be characterized as expandable, three-layer smectite-type clays having an ion exchange capacity of at least about 50 meq/100 g.

While not intending to be limited by theory, it appears that the advantageous softening (and potentially dye scavenging), benefits of the instant compositions are ascribable to the physical characteristics and ion exchange properties of the clays used therein. That is to say, experiments have shown that non-expandable clays such as the kaolinites and the illites, which are both classes of clays having ion exchange capacities below 50 meq/100 g., do not provide the beneficial aspects of the clays employed in the present compositions. Furthermore, the unique physical and electrochemical properties of the smectite clays apparently cause their interaction with, and dispersion by, the poly-anionic builder salts used in the present compositions. Thus, it has now been found that, rather than agglomerating to form viscous gels when contacted by water, the smectite clays used herein can be added to aqueous laundry baths in granular compositions containing poly-anionic detergency builders of the type disclosed herein to yield homogeneous, stable clay suspensions. The problems of gelling and agglomeration usually encountered when smectite clays are added to aqueous media in solid form are alleviated by the presence of the builder. Apparently, the negative electrical charges on the builder anions serve to repulse the clay particles, thereby providing the desired homogeneous clay dispersion and preventing agglomeration. Whatever the reason for the advantageous co-action of the detergency builder and smectite clays used herein, the combination of the poly-anionic detergency builders with the expandable, three-layer, dioctahedral alumino-silicates and expandable, three-layer, trioctahedral magnesium silicates provides a means whereby such smectite clays can be added to a surfactant-containing media in solid form to provide the homogeneous clay dispersion required for effective fabric softening.

The smectite clays used in the compositions herein are all commercially available. Such clays include, for example, montmorillonite, volchonskoite, nontronite, hectorite, saponite and sauconite. The clays herein are available under various tradenames, for example, Thixogel No. 1 and Gelwhite GP from Georgia Kaolin Co., Elizabeth, New Jersey; Volclay BC and Volclay No. 325, from American Colloid Co., Skokie, Illinois; Black Hills Bentonite BH450, from International Minerals and Chemicals; and Veegum Pro and Veegum F, from R. T. Vanderbilt. It is to be recognized that such smectite-type minerals obtained under the foregoing tradenames can comprise mixtures of the various discrete mineral entities. Such mixtures of the smectite minerals are suitable for use herein.

While any of the smectite-type clays having a cation exchange capacity of at least about 50 meq/100 g. are useful herein, certain clays are preferred. For example, Gelwhite GP is an extremely white form of smectite clay and is therefore preferred when formulating white granular detergent compositions. Volclay BC, which is a smectite-type clay mineral containing at least 3% of iron (expressed as Fe_2O_3) in the crystal lattice, and which has a very high ion exchange capacity, is one of the most efficient and effective clays for use in laundry compositions and is preferred from the standpoint of product performance. On the other hand, certain smectite clays marketed under the name "bentonite" are sufficiently contaminated by other silicate minerals that their ion exchange capacity falls below the requisite range, and such clays are of no use in the compositions of this invention.

Appropriate clay minerals for use herein can be selected by virtue of the fact that smectites exhibit a true 14Å x-ray diffraction pattern. This characteristic pattern, taken in combination with exchange capacity measurements performed in the manner noted above, provides a basis for selecting particular smectite-type minerals for use in the granular detergent compositions disclosed herein.

Optional Components.

The detergent compositions disclosed herein can contain other materials commonly used in such compositions. For example, various soil-suspending agents such as carboxymethyl-cellulose, corrosion inhibitors, dyer, fillers such as sodium sulphate and silica, optical brighteners, suds boosters, suds depressants, germicides, anti-tarnishing agents, pH adjusting agents such as sodium silicate, enzymes, and the like, well-known in the

art for use in det[illegible] compositions, can also be employed herein. [illegible]d water can also be present in said detergent compositions.

The clay-containing detergent compositions of this invention are in granular form. The compositions can be prepared by simply admixing the appropriate ingredients in dry form. The compositions are then added to water to provide a laundering liquor containing the instant compositions to the extent of from 0.02% to 2% by weight. Soiled fabrics are added to the laundering liquor and cleansed in the usual manner. The effective amount of the detergent compositions to be used will depend to an extent on the weight of clothes being laundered and their degree of soiling. Aqueous laundering baths containing said compositions provide adequate cleaning and softening benefits with soiled fabrics, especially cotton and cotton/polyester blends. The suspended clay material found in the laundering liquor also serves to absorb fugitive dye in solution, thereby reducing or inhibiting dye transfer.

The granular built detergent compositions and the fabric laundering and softening process of the present invention are illustrated by the following examples. Desized cotton terry washcloths were washed in aqueous solutions having dissolved therein various clay-containing built granular detergent compositions of this invention. Softness of the terry swatches so washed was compared with the softness of terry swatches washed in an equivalent concentration of the same built granular detergent without the clay, as well as with the softness of terry swatches washed in this same no-clay detergent solution followed by rinsing in water containing a commercially available fabric softener, Downy. Composition and solution concentrations are described in Table I below.

The terry swatches were washed for 10 minutes in a minature agitator containing two gallons of washing liquor at 120° F. and 7 gr/gal. artificial hardness. The swatches comprised 4% by weight of the washing liquor. After washing, the swatches were spun dry and rinsed with two gallons of water at 120° F. and 7 grains/gallon artificial hardness. Swatches were then dried in a conventional electric dryer.

After several treatment cycles, the test and control swatches were graded tactilely for softness by a panel of three to five judges making paired comparisons of all swatches. Graders assigned an integer grade of from 0 to 4 on a linear scale to the softer treatment of each pair, assigning the higher grades to corresponding larger differences in softness. The data obtained were analyzed statistically to obtain mean softness grades (panel score units) for each treatment and a statistical estimate of the least significant difference (LSD) at the 95% confidence level. Results of the softening tests appear in Table I.

TABLE I

Component–Wt. %	Composition No. 1	2	3	4	5	6
Anionic Surfactant*	16.8	16.8	16.8	15.3	8.4	16.8
Sodium tripoly-phosphate	32.9	32.9	32.9	45.0	24.7	49.5
Sodium Silicate	5.9	5.9	5.9	5.37	2.9	5.9
Sodium Sulphate	19.6	29.6	29.6	12.8	7.0	14.1
Miscellaneous minors	~4.1	~4.1	~4.1	~2.8	~1.6	~3.1
Gelwhite GP**	10.0					
Volclay BC***				9.1	50.0	
Moisture	Balance	Balance	Balance	Balance	Balance	Balance
Solution Concentration (wt %) of Composition	0.104	0.104	0.104	0.11	0.20	0.104
Solution pH	9.2	9.2	9.2	9.3	9.3	9.2
Rinse	Water	Water	Downy (0.07% wt.)	Water	Water	Water
Number of Cycles	4	4	4	2	2	2
Mean Softness Grade (Panel Score Units)	0.8	-2.1	0.2	-0.5	1.7	-2.6
Least Significant Difference (LSD)		0.9			1.0	

* A mixture in a 1.22:1 wt. ratio of sodium tallow alkyl sulphate and sodium linear alkyl benzene sulphonate wherein the alkyl chain of the sulphonate averages 11.8 carbon atoms in length.

** A commercially-available sodium montmorillonite clay having an ion-exchange capacity of about 100 meq./100 g.

*** A commercially-available sodium montmorillonite clay having an ion-exchange capacity of about 85–100 meq./100 g.

It can be seen from Table I that Compositions 1, 4 and 5 of the present invention provide softening benefits superior to built detergent formulations containing no clay softening agents and softening benefits comparable to those obtained with a commercial fabric softening rinse additive.

Compositions 1, 4 and 5 of the present invention also provide excellent cleaning and detergency when employed in washing solutions at the specified concentrations.

Substantially similar detergency and softening results were obtained when the anionic surfactant mixture in Composition 1, 4 or 5 (Table I) was replaced with an equivalent amount of 2-acetoxy-tridecane-1-sulphonic acid; sodium methyl-α-sulphopalmitate; sodium β-methoxyoctadecylsulphonate; sodium coconut alkyl ethylene glycol ether sulphonate or the sodium salt of the sulphuric acid ester of the reaction product of one mole of tallow fatty alcohol and three moles of ethylene oxide.

Substantially similar detergency and softening were obtained when the anionic surfactant mixture in Composition 1, 4 or 5 (Table I) was replaced by an equivalent

amount of 3(N,N-dimethyl-N-alkylammonio)-propane-1-sulphonate or 3(N,N-dimethyl-N-alkylammonio)-2-hydroxypropane-1-sulphonate wherein in both compounds the alkyl group averages 14.8 carbon atoms in length; 3(N,N-dimethyl-N-hexadecylammonio) - propane - 1 - sulphonate; 3(N,N - dimethyl - N - hexadecylammonio)-2 - hydroxypropane - 1 - sulphonate; 3 - (N - dodecylbenzyl - N,N - dimethylammonio) - propane - 1 - sulphonate; (N - dodecylbenzyl - N,N - dimethylammonio)-acetate; 3 - (N - dodecylbenzyl - N,N - dimethylammonio)propionate; 6 - (N-dodecylbenzyl - N,N - dimethylammonio)hexanoate; (N,N - dimethyl - N - hexadecylammonio)-acetate, or sodium 3 - (dodecylamino)propane - 1 - sulphonate.

Substantially similar detergency and softening were obtained when the sodium tripolyphosphate builder in Composition 1, 4 or 5 (Table I) was replaced by an equivalent amount of sodium nitrilotriacetate, sodium mellitate, sodium citrate or sodium carbonate.

Substantially similar detergency and softening were obtained when the clay softening agent in Compositions 1, 4 or 5 (Table I) was replaced by an equivalent amount of volchonskoite, nontronite, hectorite or sauconite, all such clays having an ion-exchange capacity greater than 50 meq./100 g.

In addition to the unexpected fabric softening benefits which the built laundry detergent compositions of this invention provide, there are other advantages which this invention makes possible. For instance, dye-transfer inhibition, noted above, is a significant advantage not commonly shared by ordinary fabric softening compositions.

Moreover, the particular class of clays described herein which are deposited on the fabrics, provide a soil-release benefit. The clays are adsorbed by the fabrics being washed providing an improved soil-release surface. The benefit from this treatment is that during subsequent washings, stains and soils are more easily removed from the fabrics in comparison with a fabric which has not previously been exposed to a treatment by the clay-containing compositions of this invention. Still further, all of these benefits are enjoyed without impairing the water-absorbent qualities of the treated fabric. This is in marked contrast with ordinary quaternary ammonium fabric softeners which may tend to reduce the water-absorbent property of treated fabrics after several cycles.

It is especially significant that each of the advantages described above in no way impairs or interferes with the general overall cleaning effectiveness of the detergent composition. The fact that these achievements are attained during the relatively brief span of a short washing cycle, for example from 6 to 15 minutes, is especially noteworthy.

WHAT WE CLAIM IS:—

1. A granular, built laundry detergent composition comprising:

(a) from 2% to 30% by weight of a non-soap synthetic detergent compound selected from: anionic synthetic detergents, ampholytic synthetic detergents, zwitterionic synthetic detergents and mixtures thereof;
(b) from 10% to 60% by weight of one or more organic and/or inorganic detergent builder salts; and
(c) from 1% to 50% by weight of a fabric-softening agent that is an expandable, three-layer smectite-type clay having an ion exchange capacity of at least 50 meq/100 g.,

said composition providing a solution pH of from 7 to 12 when dissolved in water at a concentration of 0.12% by weight.

2. A composition according to claim 1 which contains as component (a) from 5—20% by weight of one or more synthetic detergent compounds.

3. A composition according to claim 2, wherein as component (a) one or more anionic synthetic detergent compounds are present.

4. A composition according to any one of claims 1—3, wherein the anionic detergent is a water soluble organic sulphate or sulphonate containing an alkyl group having 8 to 22 carbon atoms.

5. A composition according to any one of claims 1—3, wherein the anionic detergent is selected from sodium linear alkyl benzene sulphonate having an average of 10 to 18 carbon atoms in the alkyl group, sodium tallow alkyl sulphate, 2-acetoxytridecane-1-sulphonic acid, sodium methyl-α-sulphopalmitate, sodium β-methoxy octadecyl sulphonate, sodium coconut alkyl ethylene glycol ether sulphonate, the sodium salt of the sulphuric acid ester of the reaction product of one mol of tallow fatty alcohol and three moles of ethylene oxide, and mixtures thereof.

6. A composition according to any one of claims 1—5, wherein the anionic detergent comprises a mixture of sodium tallow alkyl sulphate and sodium linear alkyl benzene sulphonate having an average of 11.8 carbon atoms in the alkyl group in weight ratio 1.22:1.

7. A composition according to any one of claims 1—6, which contains from 20 to 50% by weight of one or more organic and/or inorganic detergent builder salts.

8. A composition according to any one of claims 1—7, wherein component (b) is selected from: alkali metal carbonates, bicarbonates, borates, phosphates, polyphosphates, sulphates; water soluble aminopolyacetates, phytates and poly phosphonates.

9. A composition according to any one of claims 1—7 wherein component (b) is selected from sodium tripolyphosphate, sodium nitrilotriacetate, sodium mellitate, sodium citrate and sodium carbonate.

10. A composition according to any one of claims 1—9, which contains from 5 to 15% by weight of the smectite-type clay.

11. A composition according to any one of claims 1—10 wherein the smectite-type clay is selected from montmorillonites, volchonskoites, nontronites, hectorites, saponites and sauconites.

12. A composition according to claim 1 substantially as described in the Examples herein.

13. A process for the simultaneous laundering and softening of fabrics, comprising contacting said fabrics with an aqueous medium containing from 0.02% by weight to 2% by weight of a composition in accordance with claims 1—12.

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